THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 42, No. 2, 1972

INTERNATIONAL REGIONAL MEETING, AIRAPT

(*Abstract*)

The third regional meeting of International Association for the Advancement of High Pressure Science and Technology was held in the Kyoto International Conference Hall, on October 26, 1972, sponsored by the Physico-Chemical Society of Japan and supported by the 138th Committee (High Pressure), Japan Society for the Promotion of Science.

Chemical Effects and Production of High Pressures

The program was devoted to discussing the recent advancements of pressure effects on chemical reactions including kinetics, solvent effects (solvation) and polymerization (Morning session), and of the production of high pressures including multi-anvil, sliding anvil, optical devices and shock pressure (Afternoon session).

Morning session	Pressure Effects on Chemical Reactions Chairman : Prof. J. Osugi Co-chairman : Prof. K. Suzuki Invited paper : Dr. S. D. Hamann
Afternoon session	Production of High Pressures Chairman : Dr. K. Yasunami Co-chairman : Prof. S. Minomura Prof. J. Osugi Invited paper : Prof. B. Vodar

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Pressure Effects on Chemical Reactions

Pressure Effects on Reactions in Solution

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There is a growing appreciation among chemists that high pressure techniques are not necessarily difficult and expensive, and a large number of laboratories throughout the world are now using pressure as a variable in chemical reactions in much the same way as temperature has been used in the past. The speaker will review some of this work and, in particular, discuss the molecular basis of the effects of pressure on chemical equilibria and reaction rates in solution. These effects can be just as great and as varied as those more commonly brought about by changes of temperature or solvent. They will be illustrated by the results of some recent measurements of the ionization constants of substituted phenols and anilines in water at high pressures, and of the rates of some sterically hindered reactions.

The Pressure Dependence of Activation Volume

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The analysis of the pressure dependence of activation volume, $(\partial \Delta V^{*}/\partial P)_T$, in terms of ion-dielectric theory, has been performed. The values obtained on these basis are in good agreement with those found for the hydrolyses of organic halides. These results further indicate that contributions to $(\partial \Delta V^{*}/\partial P)_T$ arising from compression of the molecule or ion are by far more important than those arising from electrostriction of the dielectric medium. Also, the effects of quadrupole moments can be very important since the contributions from this are as great as those from dipole moments. Nevertheless it seems that ion-dielectric theory gives only a partial answer to the question of the nature and origin of $(\partial \Delta V^{*}/\partial P)_T$. Apparently, the contributions arising from solvent structure, unaccounted for on this model, cannot be ignored. (* not attended)

The Ionization Constants and Ionization Volumes of 2, 6-Dialkylpyridines The Effect of Pressure on Sterically Hindered Reactions

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The partial molar volumes of 2, 6-dialkylpyridines in acetone and methanol and those of the hydrochlorides in methanol are reported with pK_a values in methanol. The increase in volume in all systems are approximately 15～18 m*l* per methylene group except one case. These observations suggest the necessity to reconsider Gonikberg's theory of the effect of pressure on sterically hindered reactions. The new interpretation based on the Hammond postulate will be proposed with some other possible factors.

In addition, the reason for the abnormally large acidity of 2, 6-di-*t*-butylpyridine will be discussed.

Pressure Dependence of Solvolyses Neighboring Group Participation and Solvent Participation Pathways

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Hydrolysis of 2-aryl-2-propyl chlorides (90% aqueous acetone) and formolysis of 1-aryl-2-propyl tosylates were investigated under pressure. The observed ΔV^{*} for the 2-aryl-2-propyl chlorides showed a linear correlation with σ^{+}. This

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indicates an apparent dependence of electrostriction volume on substituents. Formolysis of 1-aryl-2-propyl tosylates consists of a solvent participated process and a neighboring group participated process (solvent assisted, k_s, and anchimerically assisted, k_Δ, respectively). From the observed rate constant (k_t), k_s and k_Δ were estimated using ρ^* in the Hammett-Taft correlation under pressure. The values of ΔV^* are linearly correlated with σ^*. However, dependence of ΔV^*_s and ΔV^*_Δ upon the substituent constants are not observed. The substituent effect on ΔV^* will be discussed.

Activation Volume in Mixed Solvents

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In general, the activation volume for chemical reaction may be regarded as the sum of two terms, *i.e.*, the structural term and the solvation one. The solvent effect on the activation volumes measured in various solvents of single component, has been almost solely explained in terms of the contribution of solvation, according to a simple form of the electrostriction theory. However, in mixed solvents including water, it is complicate and mysterious from the viewpoints of solute-solvent interaction and solvent structure. It is suggested that in such structured solvent as highly aqueous alcohol mixtures, the formation of transition state in certain reactions should require the reorientation of solvent molecules which will result in the local change of solvent environment and probably causes the decrease in volume. Therefore, it may be reasonable to take into account an additional term based on the contribution to solvent structure in understanding the activation volume measured in such a solvent. This is also supported from the consideration for the constitutive meaning in the partial molal volume of ionic substance in the same solvent system.

Solvent Effects under High Pressures

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Rate constants and activation volumes were measured for the reactions of pyridine with benzyl bromide, and of triethylamine with ethyl iodide in various solvents. The linear free energy relationships were observed in the plots of $\log k$ values of some Menschutkin reactions *vs.* $\log k$ values of the former reaction in various solvents. The activation volumes were linearly correlated to the product of the compressibility and the molar volume of the solvent. According to our proposal, the slope of the plot gives the value of $(z\Delta P)$, in which z, ΔP stand for the solvation number of the activated complex, and the average pressure within the co-sphere of the activated complex. Both slopes, expected to provide a measure of the sensitivity of the reacting system to the solvent variations, are fairly well correlated to each other. The equation which predicts the linear relation between the activation volumes and its pressure derivatives was derived. Based on the equation, the solvation number in the activated complex and the average pressure within its co-sphere have been estimated to be *ca.* 4 and 910 $kg \cdot cm^{-2}$ for the reaction of pyridine with benzyl bromide.

Pressure Effect on the Rate of *m*-Xylene Isomerization over Silica-Alumina Catalyst

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The isomerization of *m*-xylene over a silica-alumina catalyst was kinetically studied at the pressure from 300 to 6,000 kg/cm^2 and in the temperature range of 260～380°C, using the continuous flow-type high pressure equipment. Since the activation energies in the temperature range of 270～300°C for the reaction to *o*- and *p*-xylene were in good agreement with those obtained in

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the range of 350~380°C, the surface coverage of silica alumina by xylenes can be considered to be nearly 1. The activation volume obtained from the pressure dependency of the reaction rates was about -20ml/mol, its pressure dependency being rather small. From this value, together with the activation entropy of -9.4 e.u., the observed activation volume would be attributed to a shortening of the adsorption bond length, through the transfer of a proton from the position between xylene molecule and a surface oxygen ion (adsorbed state) to benzene ring of xylene adsorbed directly on a surface site (transition state).

An additional study which confirms the proposed configuration of xylene adsorbed on the surface site was also carried out and reported.

Some Considerations on Aromatic Reactions under Pressure

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Benzidine Rearrangement: The effect of pressure on the kinetics of the acid catalysed benzidine rearrangement was examined. The reaction order with H^+ was 1st order and/or 2nd order depending on the substituents. The rate constants and activation parameters were determined at elevated pressures. The volumes of activation of variously substituted hydrazobenzene are considered in terms of the electro-donating and -attracting characters of the substituents.

Rearrangement of N-Chloroacetamide: The rate constant k_0, extrapolated to zero ionic strength, is a function of the dielectric constant D of medium. The plot of $\ln k_0$ *vs.* $1/D$ should be linear with a slope of $-E^2Z_AZ_B/kTr$, where r is the distance between two ions. Rate measurement under pressure in various media will show the pressure effect on r. In the case of Orton rearranggment, apparent values of r showed no change with pressure up to 2,000atm.

Photodimerizations of Anthracene and Its Derivatives: They were studied in solution under pressure up to 3,000kg/cm^2. Changes of quantum yields with pressure were obtained. This reaction is considered as diffusion controlled.

Taking account of the pressure dependence of the life time of the lowest excited singlet state obtained from the measurement of fluorescence intensity, change of reaction rates with pressure corresponds quantitatively to the change of reciprocal of solvent viscosities with pressure.

The Penultimate Effect on Copolymerization under High Pressure

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Several copolymerization systems must have been considered that the reactivity of a growing chain in copolymerization might be influenced by the nature of the remote monomer units, which has been proposed as the penultimate effect on copolymerization. Accordingly, unusual pressure effect have been expected on these copolymerization systems because the volume of transition state would be abnormally large in order to interact between remote unit of polymer radical and monomer.

On these copolymerization systems, the copolymer compositions calculated from the penultimate or pen-penultimate model equation satisfactorily represent the experimental results and the copolymer compositions are affected by pressure. High pressure is presumed generally to be effective for the eliminating the penultimate effect on these copolymerization.

The Properties of Polymer Solutions under Pressure

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Most of the work described in this lecture has

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been done at Uppsala during the last ten years.

First our experimental technique will be discussed. Portable cells with windows for observation up to 8,000 atm have been designed.

For solutions of polystyrene may be mentioned: the change in virial coefficient with pressure $(\partial A_2/\partial P)_T$, which theoretically depends on ΔV, can be related to the heat of mixing of the polymer for simple systems. Solutions with exothermic heats of mixing give a positive increase in the virial coefficient which levels off at high pressure. Endothermic solutions give a decrease leading eventually to precipitation.

- The pressure dependence of the virial coefficient varies strongly with the composition in solvent mixtures.
- The molecular weight dependence of $(\partial A_2/\partial P)_T$ in both exothermic and endothermic systems is substantial.
- Measurements of the Rayleigh ratio as a function of pressure are also reported.

Quasi-elastic light scattering measurements give the pressure dependence for the diffusion coefficient and accordingly the frictional factor. Both polymers and proteins have been studied.

Effect of Pressure on Hydrolysis of Esters by Polymer Sulfonic Acids

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The hydrolysis rates of aliphatic esters (methyl-, ethyl-, *n*-butylacetate) by polystyrene sulfonic acids were found to be decreased by pressure. The volume change of activation (ΔV^*) accompanying the hydrolysis showed to be positive and the values increased with both increase of hydrocarbon parts of esters and the decrease of the sulfonation degree as catalysts. These results seem to correspond to the strength of the hydrophobic interactions between esters and polymer catalysts.

While, the hydrolysis rates of esters by *ortho*-benzal sulfonated polyvinyl alcohols were accelerated by pressure. The absolute values of ΔV^*, which was the negative sign, decreased with increasing both hydrocarbon parts of esters and the degree of the sulfonation.

These differences of hydrolysis of esters under pressure will be explained by the volume changes accompanying the intermolecular interactions between substrates and catalysts.

Pressure Effects on Hydrated Ions

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The conductivity of electrolytes in aqueous solution has been measured under high pressure. The results of the following subjects will be discussed.

Ion-Pair ⇄ Free Ion Equiribrium: We can get the dissociation constants of various kinds of ion-pairs under high pressure, by which the molar volume change in the dissociation process, ΔV°, and the colsest approach distance of ion-pairs, $\hat{a}$, according to the Fuoss theoretical equation, are calculated. ΔV° and $\hat{a}$ offer informations about the solvation (hydration) of ion-pairs. Such ion-pairs as $[Co(NH_3)_6]^{3+}\cdot SO_4^{2-}$, $Mg^{2+}\cdot SO_4^{2-}$, $Ca^{2+}\cdot SO_4^{2-}$, $[Co(NH_3)_5NO_2]^{2+}\cdot SO_4^{2-}$ and $Ni^{2+}\cdot SO_4^{2-}$ have been studied.

Ion-Water Interaction: The conductivity measurement is one of the most effective methods to study the ion-solvent interaction, since the limiting equivalent conductance, Λ°, can be divided into the individual limiting ionic conductance, λ_i°, with the aid of the transference number, t_i°. We have determined t° (K^+) in KCl by the moving boundary method up to 1,500 kg/cm^2. Also, the limiting equivalent conductances under high pressure, $\Lambda^{\circ(P)}$ have been measured on $[Co(NH_3)_6]_2(SO_4)_3$, $MgSO_4$, $CaSO_4$, $[Co(NH_3)_5NO_2]SO_4$, $NiSO_4$, KCl and R_4NCl in water.

We can estimate the ion-solvent interactions of each ion through their hydration numbers or the Walden products.

Pressure Effect on The H_2-O_2 Flame

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In order to investigate the structure of the flame under pressure the usual technique for studying the flames was combined with the technique of the propellant motors (where the combustion chamber pressure is about 25 atm).

The flow reactor is a quartz tube, I. D. 2 cm, concentric with a second quartz tube for water cooling. The quartz allows optical measurements; we have measured the temperature through the reversed-line method and the OH radical concentration spectroscopically; but at the same time pressure is limited; we have attained 12 atm at 3300°K.

Furthermore other quantities are measured: flow velocity, gas enthalpy and non-radical species composition, utilizing the same probe, which is water cooled and designed with a nozzle for expanding the sampled gas and freezing the composition.

The compositional, flowdynamic, enthalpic and thermal profiles are obtained; at the same time one may observe as far as the pressure is increased that the flame front thickness is decreased, while the radiant energy is increased. The thermal profile shows two maximums related to the reaction stages.

The radical chain reaction kinetics, as adopted for close vessel or flow reactor at low pressure, cannot be fully applied. The mechanism is changed; even this elementary reaction, H_2+O_2, is remarkably influenced by the pressure.

On the Pressure-Induced Organic Reactions

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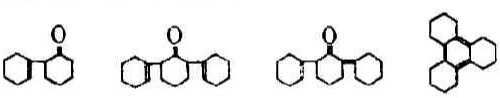
Reactivity of nitriles, ketones and aldehydes under high pressure has been investigated. The aspects considered are i) the influence of the characteristic properties of functional groups: cyano- and carbonyl-groups, ii) the influence of molecular species in the reactants and iii) the effects of pressure on the critical reaction conditions such as ceiling temperature or floor temperature.

Polymerization of Nitriles: Linear polymers with carbon-nitrogen conjugated chain:

$$-(-\underset{|}{C}=N-)-_n$$

have been obtained under high pressure above *ca.* 20kb from the polymerization of cyano-groups in dinitriles such as malono-, succino-, glutaro- and adiponitrile. The products are thermally stable and insoluble. While dimethylmalononitrile, which has no α-hydrogen, is hardly to polymerize. This shows that the existence of α-hydrogen plays an important part in these reactions.

Condensation of Ketones: Several ketones undergo condensations at pressures above 20kb and temperatures above *ca.* 160°C without catalyst. In a condensation of cyclohexanone, four products confirmed are:



(Ⅰ) (Ⅱ) (Ⅲ) (Ⅳ)

The structure of products seems to suggest the existence of a keto-enol type equilibrium and the increase in the enol form at high pressures. The yield of (IV) increases as the pressure and the temperature are raised.

In both of these reactions in nitriles and ketones, the reactivity comes from a strong polarization of functional groups; cyano- and carbonyl-groups, so that the α position plays an important contribution to the reactions. The rates of both reactions are very fast and the rather clear-cut conditions to cause the reactions like "floor temperature" are observed at high pressures.

Polymerization of Aldehydes: *n*-Butyr-, *iso*-butyr- and propionaldehyde with catalyst DPPH appear to undergo the somewhat different polymerization to give a polyacetal type polymer at

5,000~8,000 atm and 5~40°C. From the pressure dependence of the ceiling temperature, the pressure dependences of the thermodynamic parameters accompanying the polymerization are derived.

Solid-State Reactions in Some Organic Charge Transfer Complexes under Super High Pressures

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The electrical resistance of some organic charge transfer complexes was measured up to several hundred kilobars in a split sphere apparatus. In the following complexes the irreversible rise in resistance was observed; *p*-phenylenediamine-chloranil (PD^+-CA^-), N, N-dimethyl-*p*-phenylenediamine-chloranil ($DMPD^+$-CA^-), N, N, N′, N′-tetramethyl-*p*-phenylenediamine-chloranil ($TMPD^+$-CA^-), dimethylaniline-chloranil (DMA-CA), *p*-phenylenediamine-bromide (PD^+-Br^-) and *p*-phenylenediamine-perchlorate (PD^+-ClO_4^-). On the other hand the resistance of potassium-chloranil (K^+-CA^-), Wurster's red perchlorate (WRP) and Wurster's blue perchlorate (WBP) decreased monotonously. The irreversible effect was attributed to the chemical reaction occurring in the solid state from the inspection of the UV, visible, and infrared absorption spectra, and also the ESR spectra, of the recovered samples after compression. At extremely high pressures the possibility of polymerization may be expected.

Electrochemical Reactions of Ferrocene Derivatives at High Pressures

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The activation volume and the diffusion constant of ferrocene derivatives for the electrochemical reaction were measured at high pressures up to 1,000 atm.

The cyclic current step (c. c. s.) method was used for the measurement of the exchange current density. The low-frequency rectangular current was applied to the platinum micro-electrode dipped in a methanol solution containing ferrocene-ferricinium couple.

Ferrocene has the apparent activation volume of about −10 cc/mole for the electrode reaction and its diffusion constant augments with the increase of pressure.

Production of High Pressures

Sliding Anvil and Low Temperature Optical Device

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These presentation describes briefly the recent developments of two apparatus at the CNRS laboratory at Bellevue.

A prototype of sliding anvils, developed by R. Epain and Mme Loriers-Susse have been constructed in the type 1 design comprising 4 anvils sliding in one plane and two stationary anvils, the initial volume of the cell being 372 mm^3. Teflon or mica foils were used for reducing friction with talc or AgCl as pressure media. Calibrations were successfully made from electrical conduction measurements on Bi I-II, Bi III-IV, Ba I-II and the upper transition of Sn. It was demonstrated that there was no appreciable extrusion and that the displacement of an anvil permitted to determine volumetrically phase transitions, because of an increase sensitivity due to a differential effect

of the 2 sets of anvils (for example the ΔV of Bi I-II was measurable with only about 4 mm^3 of Bi in the cell).

In concluding the main advantages of this type of apparatus are stressed: tightness against loss of matter, sensitivity to volume changes, in principle no limitation of the useful stroke and therefore independance of the pressure reached from the volume used, good lateral compression permitting increase the elatstic behaviour of materials to higher loads.

An optical cell for infrared studies up to 14 kb at 2°K was developed by Dr. Marteau and Dr. Vu Hai: the pressure can be varied at low temperatures as it is produced by a piston actuated by a press kept at room temperature; the moving seals, made of potassium metals, proved very satisfactory; the cell made of copper beryllium alloy is equiped with sapphire windows. Infrared pressure induced spectra of H_2 and D_2 are reported; a strong increase of their intensity was noted when the density of solid H_2 is increased two fold; shifts in the phonon bands are about 10 times larger than in those of quadrupole bands. Such results provide interesting checks of theoretical calculation of the behavior of molecular solid hydrogen in view of foreseeing the transition into metallic hydrogen.

Mechanisms and Mechanics of High-Pressure-Generating System

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A study of the high-pressure-generating system is made and the discussions are presented as to what is most appropriate for generating extremely high static pressure. The essential points to reach the higher pressures are (1) the suitable combination of mechanism for supporting the components such as anvils of the pressure-generating system, and the way of the pressure intensification, (2) the mechanism having the unlimited stroke of the components of the system to compress the pressure medium and (3) the bigger press to confine larger volume.

The optimum mode of the pressure intensification and of the supporting the components of a system is presented. A possibility is suggested for generating the extremely high pressure in a very large volume by using the finite strength of material, provided that we have a very big press with very large allowance. As for the second point, the most promising one is supposed to be the MASS (Multiple-Anvil Sliding System) of three dimensional geometry.

Several different types of MASS apparatus under developement in Japan are presented together with the data of the test experiments up to 200 kb or more.

Kobe Steel Type Super-High Pressure Apparatus and Its Modification

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A characteristic of Kobe Steel type super-high pressure apparatus is that it can produce pure hydrostatic pressure in the material by the six anvils uniformly advanced by the surfaces inclined at an angle of 45° to the vertical axis of the apparatus. In order to spread a zone of uniform temperature in the sample material, we have studied to modify the shape of sample chamber from cube usually used to a quadrilateral prism. In the modified configuration, we have made a tentative calculation on the pressure and temperature distribution in the sample material under the super-high pressure conditions.

Cubic Anvil X-Ray Diffraction Press

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Cubic anvil X-ray diffraction press were developed, with which powder diffraction patterns of substances at pressure up to 100 kb and tem-

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perature to 1,000°C can be obtained.

Debye-Scherrer powder diffraction geometry were adopted in this apparatus. Mo $K\alpha$ characteristic X-rays are introduced through one of the gaskets of cubic anvil apparatus and impinged upon sample at the center of cubic pressure medium made of amorphous boron filled plastics composite material. Diffracted X-rays through the opposite gasket are detected with NaI (Tl) scintillation counter. Diffraction patterns are recorded by fixed-time-counting method using step-scannable goniometer in order to obtain good counting statistics. Consequently lattice parameter can be determined within error of 0.1%. Compressibility measurements of some alkali halides, oxides and intermetallic compounds are reported as an example of use of this cubic anvil X-ray diffraction press.

The Link-Type Cubic Anvil, High Pressure-High Temperature Apparatus

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In the link-type cubic anvil apparatus, which was developed by Toshiba-Tungaloy Co., Ishikawajima-Harima Heavy Industries Co. and Toshiba R & D Center in cooperation, a uniaxial force from a usual oil press is converted into triaxial forces by a frame structure consisting of movable links. Geometry of the link mechanism ensures synchronized and equal compression by the vertical and the lateral anvils in a sufficient accuracy. A very accurate alignment of anvils is achieved and maintained throughout hundreds of successive usages. Pressure is elevated reproducibly up to the Bi (3→5) and the Sn transition pressures, with 10 mm- and 6.4 mm-edged anvils, respectively. Further, by correcting the effect of elastic deformation in structural parts, anisotropy is completely eliminated both in anvil movements and in generated pressure. Temperatures higher than 2,000°C are attained in a heating element, 4 mm in diameter and 8 mm long, while anvil-temperatures do not exceed 300°C. Performance of the apparatus will be discussed in details, together with some experiences of practical use in high pressure synthesis research.

On a Multi-Stage Split Sphere Apparatus for High Pressure Production

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6-8 Double Stage Anvil Type High Pressure Apparatus

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The apparatus which can generate the pressures more than 200 kb has developed. This apparatus consists of eight cubes which act as 2nd stage anvil and six 1st stage anvils surrounding the 2nd ones. The 2nd stage anvils, the corners of which are cut, form the octahedral pressure space. Anvils are shielded within rubber shell and drived simultaneously by oil pressures. In the pressure space, pyrophyllite octahedron is inserted as a pressure media. According to the scaling low examination, the obtainable pressure and temperature depend on the volume of the pressure space. When the octahedron of 8 mm in edge length is used, the maximum pressure and temperature will exceed 200 kb and 3,000°C, respectively. The generated pressures are calibrated against the oil pressures at both room temperature and high temperatures. As the pressure standard, electrical conductivity transitions of Bi, Ba and Pb are used at room temperature and the phase transitions of cobalt silicate and silica are used for high temperatures. Pressures at high temperatures are slightly higher than those at room temperature for same oil pressure. Many high pressure transformation experiments have been made.

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Test of Large Bridgman-Type Anvil

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The pressure distribution within a gasket squeezed between Bridgman anvils is expected to be the same if the ratio of diameter to thickness remains constant. Previously relations connecting the final thickness of pyrophyllite disc, the load and the pressure were obtained for Bridgman anvil of 26mm diameter. From the analysis it was found that up to 80kb the shear stress, maximum shear strength of pyrophyllite, varies with pressure linearly. Above 80kb the efficiency of pressure generation diminishes with increase of loads. Test were also done with Bridgman anvils having center flat of 78mm diameter, the central part being 50mm diameter WC cylinder surrounded with SKH steel ring. Up to 80kb the relation between generated pressures and applied loads is perfectly similar as in the case of 26mm diameter anvils. Above 80kb the efficiency of pressure generation diminishes as before and the remnant thickness of gasket is nearly constant. The Ba (2–3) transition was not observed under the load of less than 950 ons.t From these facts it is considered that above 80kb pyrophyllite does not flow plastically and the actual shear stress is smaller than the maximum shear strength by far.

High Pressure Studies Using a Diamond Anvil Device

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Corporate Research and Development
Tokyo Office

The use of the small and compact diamond anvil high pressure cell allows the scientist to perform high pressure experiments with a rather modest investment for equipment. The size of the device permits optical, X-ray and spectroscopic measurements to be made quite easily. By applying gasketing techniques and utilizing a fluid pressure transmitting medium, it is possible to obtain nearly hydrostatic pressures. The degree of hydrostaticity can be measured by observing X-ray line broadening. The use of gem type diamonds produces a clear optical path which allows optical observation of high pressure phase transitions as well as the measurement of changes in the absorption properties.

X-ray optical and spectroscopic measurements up to approximately 150kb have been made using a diamond anvil device.

Effects of Shear on Growth of Coesite under High Pressure

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Crystal growth of coesite under high pressure depends strongly on the starting material and also on the experimental condition. The processes of crystal growth of coesite from amorphous silica, crystoballite and quartz were investigated. A girdle-type high pressure apparatus was used. The starting material of about 50mg, which was added about 10% of distilled water or sodium hydroxide solution, was heated at 910°C under 30kb for various times. The process of growth of coesite was found to be determined from many factors, relaxation of stress in the sample which may be induced from external shear, solubility of the sample into solute and stress gradient in the pressure cell.

Oriented Growth of Graphite in Pressure Sintered Carbons

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** *Faculty of Engineering, Mie University/Japan*

Carbons, even non-graphitizing carbons, have been found to be sintered and graphitized at about 1,500°C under the pressure of 5kb. The remarkable increase in density and the neck formation were shown by using small spherical particles of carbon. The graphitization initiated

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at the contact points. in other words, stress concentrated parts, of the particles and to grow into mitrix. The growth of graphite was found to be oriented, being its basal plane parallel to the stress gradient, from the observation by the polarized light microscopy. By scanning electron microscope, the same conclusion was obtained.

Shock Wave Techniques

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Shock waves from explosions are capable of prducing pressures very much higher than any that can be reached by static methods at the present time. For instance, Trunin and his colleagues in the Soviet Union have recently succeeded in measuring the densities of some metals at shock pressures as great as 50 Mbar ($=5\times10^{12}$ P_a).

Shock wave techniques have the added advantage (for some purposes) of combining high pressures with very high temperatures, so that some chemical reactions that are normally very slow occur in less than one microsecond in strong shock waves. However, the techniques have the disadvantages that the shock conditions are very short-lived; that it is not easy to vary the tempeature independently of the pressure; and that it is extremely difficult to recover a specimen intact after it has been strongly shocked.

The speaker has used shock wave methods to study: (a) the chemistry and physics of water and aqueous solutions at pressures up to 300 kb and temperatures of several thousand degrees Kelvin, (b) the chemistry of non-aqueous solutions under similar conditions, (c) shock-induced polymerizations of solids and (d) "metallic transitions" of insulators. Some remarkable changes have been found.

Isostatic Pressure Production by Using Molten Glass or Salt as a Pressure Transmitting Medium

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Some techniques for hot isostatic pressure production by using molten glass or salt as a pressure transmitting medium were developed for hot isostatic compaction of powder compacts. Low viscous and poorly reactive materials at desired high temperature were used for pressure transmitting medium. Three methods for this purpose were tried as follows.

(1) Powder compacts were compressed in graphite die with molten glass or salt. Maximum temperature and pressure are 1,800°C and 0.3 kb.

(2) Powder compacts were compressed in an inner graphite heater in a piston cylinder type high pressure device. Maximum temperature and pressure are 1,600°C and 50 kb.

(3) Powder compacts with molten pressure medium were compressed dynamically for a very short time. High dense semi-sintered compacts can be obtained by this method. Very high dense sintered bodies can be produced easily by heating of the above compacts at atmospheric pressure. Some properties of these media are discussed.

Production of High Liquid Pressure by Using a High Speed Hammer and Its Application to Industry

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In 1966, a prototype machine was built by Tokyu Car Manufacturing Co. to generate impulsive hydraulic pressure of several thousand atmospheres. Since then, extensive improvements have been tried and completed on the operational reliability and durability. A series of versions have been turned out as models of shockless design, of higher pressure, of longer duration, and of larger energy output.

The machine functions in the following manner. In a vertical cylinder, a hammer is accele-

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rated by compressed air. A plunger integral with the hammer is plunged into liquid in a pressure chamber. Kinetic energy contained in the high speed hammer is imparted to the liquid to generate hydraulic pressure, which useally lasts several milliseconds.

High pressure thus produced is applicable to high-energy-rate forming, high speed powder compaction, water jet working, *etc.* As an example, forming machines consisting of this pressure generator coupled with an automated forming die set are now widely used for mass production of machine parts, such as automobile bearing spacers, V-belt pulleys, shock absorber elements, push rod covers, and pipe fittings.

Capable of producing high pressure with safe and easy operation, the pressure generator is expected to contribute to various field of science as well as industry.